

AD-A142 879

FORMATION OF SILICIDE CONTACTS USING CODEPOSITED
REFRACTORY METALS ALLOY. (U) TECHNION RESEARCH AND
DEVELOPMENT FOUNDATION LTD HAIFA (ISRAE.
M EIZENBERG ET AL. JAN 84 DAJA45-83-C-0013 F/G 9/1

1/1

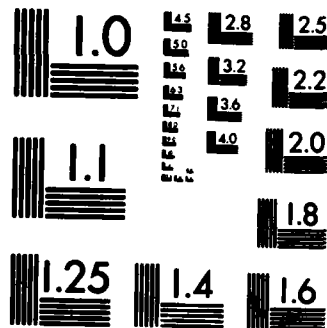
UNCLASSIFIED

NL

END

FILMED

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A142 879

AD

(12)

FORMATION OF SILICIDE CONTACTS USING CODEPOSITED
REFRACTORY METALS ALLOY FILMS

Final Technical Report
for the period : January-December 1983

by
Dr. Moshe Eizenberg and Ami Appelbaum
January 1984

United States Army
EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY
LONDON - ENGLAND

Contract Number : DAJA 45 - 83 - C - 0013

DTIC
SELECTED
JUL 03 1984
E

TECHNION RESEARCH AND DEVELOPMENT FOUNDATION LTD.
HAIFA - ISRAEL

Approved for public Release ; distribution unlimited.

84 07 02 004

DTIC FILE COPY

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

R&D 3094-MS

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A142899	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Formation of Silicide Contacts Using Codeposited Refractory Metals Alloy Films		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Dr. Moshe Eizenberg and Ami Appelbaum		8. CONTRACT OR GRANT NUMBER(s) DAJA45-83-C-0013
9. PERFORMING ORGANIZATION NAME AND ADDRESS Technion Research & Development Foundation Ltd, Haifa, Israel		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 6.11.02A IT161102BH57-04
11. CONTROLLING OFFICE NAME AND ADDRESS USARDSG-UK Box 65, FPO NY 09510		12. REPORT DATE Jan-Dec 83
		13. NUMBER OF PAGES 31
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Silicides, Thin Films, Alloy Films, Contact reaction, Metal-semiconductor interface, Interdiffusion		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Contact reactions of a Si substrate and thin films of co-deposited two refractory metals have been studied. Three systems have been chosen Ta-V, Ta-W and Ti-V. As reference also two bilayer structures for each system have been studied (e.g. Ta/W/Si and W/Ta/Si for the Ta-W system). In each system the dependence of the interaction with Si on annealing temperature and on alloy composition is investigated. The interdiffusion and silicide formation have been analyzed by Auger electron spectroscopy and X-Ray diffraction. ←		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Since both alloy constituents are refractory metals for which silicide formation is controlled by Si outdiffusion, the interaction of these alloys with Si is expected to maintain the uniform components distribution without phase separation. And indeed this is observed for the Ta alloys. On the other hand for the Ti-V alloys, Ti accumulation at the substrate is found. The great affinity of Ti to form a silicide is manifested in the case of the bilayer structure of Ti/V on Si when Ti atoms from the outer region penetrate through the inner V layer and form titanium silicide at the Si interface.

For the alloys studied mutual solubility of both constituents is observed for the as-deposited state and this stabilizes the film and delays silicide formation to higher temperatures. Even the fully reacted films in most cases show mutual solubility of the silicides, e.g. for $Ta_{50}V_{50}$ only $TaSi_2$ reflections without those of VSi_2 are observed. Alloying stabilizes also at the earlier stages of reaction metal rich silicides (e.g. Ta_5Si_3) that are usually not observed for single refractory metal interaction with Si. No ternary compounds were observed for any of the studies systems.

Accession For	
NTIS CTR	<input checked="" type="checkbox"/>
DTIC TAB	<input checked="" type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Table of Contents

1. Introduction
 2. Experimental Procedures
 3. Results
 - 3.1 Ta-W
 - 3.1.1 Bilayer Structures
 - 3.1.2 Alloy Films
 - 3.2 Ta-V
 - 3.2.1.1 Bilayer Structures
 - 3.2.2 Alloy Films
 - 3.3 Ti-V
 - 3.3.1 Bilayer Structures
 - 3.3.2 Alloy Films
 4. Discussion
 - 4.1 Structure of the As Deposited Films
 - 4.2 Reaction Temperatures
 - 4.3 Reaction Products
 - 4.4 Components Distribution
 5. Summary
- References
- Tables
- Figures

1. Introduction

Silicides of transition metals are commonly used in the microelectronic industry as ohmic or rectifying contacts on the one hand and as gate electrodes and interconnection lines in MOSFET technology on the other hand. For the latter use the refractory metal silicides are utilized due to their low electrical resistivity and their ability to withstand high temperatures, chemical treatments and thermal oxidation⁽¹⁾. Recently attention has been drawn to multi-component metal systems (alloys and bilayers) on silicon, because of their potential use for forming shallow contacts on devices whose size is shrinking, to tailor the Schottky barrier height and to establish a reliable barrier against Al penetration to the contact area⁽²⁾. Extensive work has been done studying Si and near noble-refractory metal alloys interactions that result in phase separation;⁽³⁻⁸⁾ the silicide of the near noble metal (Pd, Pt or Ni) is formed adjacent to the substrate while the refractory metal (W, V, or Cr) is found in the outer layer. This phenomenon has been explained in terms of the differences in the mechanisms of silicide formation for the two groups of metals. On the other hand very limited work has been published on the reaction between Si and alloys consisting of two refractory metals⁽⁹⁻¹¹⁾. In order to obtain a better understanding of the metallurgical phenomena involved in such thin alloy film - silicon reactions, we have investigated three systems of refractory metals alloys: Ta-W, Ta-V and Ti-V. Ta and Ti have been chosen since their silicides are currently used in VLSI technology; V and W have been selected as the alloying agents, the first one reacting with Si at much lower temperatures than the second one.

The separate behavior of each of the metals on Si is documented⁽¹²⁾. For V, Ta and W only one type of silicide (the disilicide) is formed at temperatures above 600, 650 and 700°C respectively, while for Ti- the disilicide formation is preceded by the appearance of TiSi at ~500°C. Although this study is focussed on alloy films, we have prepared also bilayer films of Ta/W, W/Ta, V/Ta, Ta/V, Ti/V and V/Ti on Si. This was done for two reasons: 1) as reference to observe the behavior of each metal on Si under our deposition and annealing conditions (recalling that refractory metal films are very sensitive to impurities such as O or C). 2) to study the interdiffusion between the two metals of an alloy film.

2. Experimental Procedures

n-type Si wafers with resistivity of 1-10 Ω .cm and <100> orientation were etched in buffered HF, rinsed in DI water and dried before being loaded into an evaporation chamber operating at 10⁻⁸ Torr. The metal films were deposited using electron beam evaporation. The bilayer structures were produced by sequential deposition, whereas for the alloy films codeposition was utilized. The alloy films of Ta_xW_{100-x}, Ta_xV_{100-x} and Ti_xV_{100-x} were prepared in three nominal compositions: x = 20, 50 and 80. The thickness of the films was 1000-2000 Å. Annealings (unless other specified of 30 minutes duration) were performed in an evacuated quartz-tube furnace maintained in a vacuum lower than 3 x 10⁻⁶ torr.

Two complementary techniques were used to analyze the films in the as-deposited state and following the heat treatments. Component distribution was determined by Auger electron spectroscopy (AES) in a PHI 590A system using a primary beam of 3-4 KeV, 1-2 μ A electrons and combined with 4 KeV Ar⁺ ion etching for depth profiling. Phase identification was carried out by X-Ray diffraction in a standard Phillips powder diffractometer equipped with a stepping motor, controlled and monitored by a 4051 Tektronix minicomputer; detection periods of 20 sec and 0.1^o steps (in 2 θ) were utilized.

3. Results

3.1 Ta-W

3.1.1 Bilayer Structures

The AES depth profile of Ta/W/Si in the as-deposited state is exhibited in Figure 1. The vertical ordinate denotes the Auger peak-to-peak height which is assumed to be proportional to the atomic concentration of each element, whereas the abscissa expresses the sputtering time which corresponds to the film thickness.

Heat treatment up to 750°C (30 min) did not show any change in the profile, i.e. tungsten did not react with the substrate and no interdiffusion took place between tungsten and tantalum.

Following an 850°C anneal the solid state reaction with Si has been observed, as is exhibited in Figure 2. One can note Si penetration through all the W layer and most of the Ta layer; only at the outermost region the reaction is hindered by carbon that probably has diffused inwards from the annealing atmosphere. The X-Ray diffractogram of this specimen is presented in Figure 3. All the peaks match very well the reflections of TaSi_2 ⁽¹³⁾ and WSi_2 ⁽¹⁴⁾. Thus, we confirm earlier reports⁽¹²⁾ that W and Ta directly form on a Si substrate their end product-the disilicide. The formation temperature of WSi_2 is 800-850°C (for a 30 min annealing period) and TaSi_2 is not observed at lower temperatures since the Si atoms must first react with the W layer before encountering the Ta layer.

In the case of the other bilayer, that of W/Ta/Si, TaSi_2 was formed as expected following the 750°C heat treatment. At this temperature the W layer remains intact and it transforms to WSi_2 only after annealing at 850°C, which is similar to the above mentioned behaviour for the Ta/W/Si structure.

3.1.2 Alloy Films

Three alloys of Ta_xW_{100-x} ($x=20, 50$ and 80) have been investigated. The distribution uniformity of the components in the as-deposited films is observed in the AES depth profiles. The X-Ray diffraction patterns reveal BCC structures with lattice parameters increased with x , as is exhibited in Fig.4 for the (110) reflection. (It is noted that both metals have a BCC structure).

The initiation of the reaction of $Ta_{80}W_{20}$ with Si is observed after the $750^{\circ}C$ anneal and it is completed following the $850^{\circ}C$ -30 min heat treatment. The AES profile of this sample is depicted in Figure 5. One can observe that along most of the profile, (i.e. for sputtering times longer than 22 min) both W and Ta react uniformly with Si without significant accumulation of one of the components. In the outer region there is some carbon accumulation followed by an increase in the Ta signal and a decrease in that for Si. In this region also, as with the situation indicated by Figure 2, silicide formation is retarded by the presence of carbon.

The X-Ray diffractogram of the $Ta_{80}W_{20}$ sample following the $850^{\circ}C$ anneal is exhibited in Figure 6. Most of the peaks match very well the reflections of $TaSi_2^{(13)}$ and coincide with the corresponding peaks in the annealed bilayer structures (see Figure 3). However, there are five new peaks that do not appear in Figure 3 and which do not match the reflections obtained for WSi_2 and $TaSi_2$, but they match perfectly the strong reflections of $Ta_5Si_3^{(15)}$. The latter is a phase that is usually not observed for reactions between a thin film of Ta and a Si substrate. Thus

we detect TaSi_2 and Ta_5Si_3 without any indication for the presence of WSi_2 . The higher temperature processing (950°C) maintains a similar depth profile, but the Ta_5Si_3 peaks disappear.

The AES analysis of the $\text{Ta}_{50}\text{W}_{50}/\text{Si}$ sample annealed at 750°C reveals that no reaction has yet occurred, although for pure Ta or for the Ta-rich alloy silicidation is taking place at this temperature. Interaction with the substrate is observed following an anneal at 850°C ; both metals react uniformly with Si without accumulation of one of the components. X-Ray analysis of this sample exhibits only reflections of TaSi_2 , without a sign to reflections of W or its silicide. The higher temperature processing of 950°C maintains a uniform in-depth distribution of the elements, but now in the X-Ray pattern WSi_2 reflections are added to those of TaSi_2 .

For the W-rich alloy composed of $\text{Ta}_{20}\text{W}_{80}$ no contact reaction with Si is observed even after 2hrs. annealing at 850°C . Impurities, either in the film or primarily at the Si substrate interface, that could hinder the expected reaction, could not be detected (to the limit of the AES technique). The interaction with Si is observed following annealing at 950°C for 30 min. The AES analysis reveals a fully reacted layer (Si reaches the surface) with a uniform in-depth distribution of the elements. By X-Ray diffraction the presence of the expected WSi_2 and the metal rich $\text{W}_5\text{Si}_3^{(16)}$ is identified.

3.2 Ta-V

3.2.1 Bilayer Structures

The reaction of the bilayer structures Ta/V and V/Ta with Si was examined using Auger analysis technique. For Ta/V on Si, the reaction of V with Si occurs at 650°C , while the reaction of Ta with Si (for both

structures) is observed at 750°C. The phases are VSi_2 and TaSi_2 , respectively. However, intermixing of metals does not occur in heat treatments up to 850°C.

3.2.2 Alloy Films

Three alloys of $\text{Ta}_x\text{V}_{100-x}$ ($x=20, 50$ and 80) have been investigated. The distribution uniformity of the components in the as deposited films was observed in the Auger depth profiles. Similarly to the case of Ta-W the X-Ray diffraction patterns reveal BCC structures with lattice parameters increased with x (again it is noted that both metals have a BCC structure).

For the $\text{Ta}_{80}\text{V}_{20}$ alloy no reaction is observed after a 650°C annealing, the temperature where VSi_2 is formed for Ta/V/Si. Partial reaction is observed following an annealing at 750°C, as can be observed in Fig. 7. The reaction is completed after a 850°C heat treatment. No preferred accumulation of one of the elements is observed in the AES profiles. The phases identified by X-Ray diffraction are $\text{TaSi}_2^{(13)}$ for the 750°C anneal and TaSi_2 plus Hexagonal $\text{Ta}_5\text{Si}_3^{(15)}$ for the 850°C anneal. The Ta-rich silicide, that is not detected in annealed Ta films on Si, is the same phase reported above for the $\text{Ta}_x\text{W}_{100-x}$ alloys.

$\text{Ta}_{50}\text{V}_{50}$ starts reacting with Si at 750°C. X-Ray diffraction yields a set of reflections that are attributed to two Ta_5Si_3 phases (hexagonal ⁽¹⁵⁾ and tetragonal ⁽¹⁷⁾) and to TaSi_2 structure with a slightly distorted lattice parameter (this will be explained in sect. 4.3 by the formation of a solid solution of TaSi_2 and VSi_2). The reaction is completed following a heat treatment at 850°C. The metal rich silicide disappears and the reflections of TaSi_2 are shifted even more. The vanadium rich alloy $\text{Ta}_{20}\text{V}_{80}$ reacts with Si

forming VSi_2 already after a heat treatment at 650°C for 30 min. For this alloy as for all other $\text{Ta}_x\text{V}_{100-x}$ films no accumulation of one of the elements is observed by the AES depth profiling.

3.3 Ti-V

3.3.1 Bilayer Structures

V/Ti and Ti/V bilayers on Si have been investigated. The deposited products are two separate layers of V and β -Ti (a BCC phase obtained in bulk material only at high temperatures⁽¹⁸⁾). A very small amount of Ti in the V film is found already at the as-deposited state, probably indicating some accumulation at grain boundaries. For both bilayers Ti diffuses through the V layer during the anneal at temperatures equal to or higher than 650°C . In both cases Ti is oxidized on the surface and forms a silicide at the Si-metal interface, showing a rapid transport of Ti through the V film. This is exhibited for Ti/V/Si annealed at 750°C in Fig. 8, where we see the titanium oxide and titanium silicide accumulations for sputtering times 0-8 and 50-65 min., respectively. The identified phases are VSi_2 and TiSi.⁽¹⁹⁾ The TiSi_2 ⁽²⁰⁾ which is expected to form at this temperature, is not detected. For the opposite structure of V/Ti on Si the penetration of Ti through the V and oxidation on the surface is much smaller (Fig. 9); the reaction with Si starts at $\sim 550^\circ\text{C}$. The 850°C annealed sample (Fig. 9b) is well behaved - a uniform reaction with V (resulting in VSi_2 formation) and with Ti (resulting in TiSi_2 + some TiSi) is observed. On the other hand for the 750°C annealing (9a) the V region is non uniform - a dip in the Si signal accompanied by a pile-up of V and C is observed for sputtering times of 4-10 min. The phases identified by X-Ray are V_5Si_3 ⁽²¹⁾ and TiSi plus TiSi_2 .

A metal rich phase for Ti is also identified - for the 650⁰ C heat treatment $Ti_5Si_3^{(22)}$ plus TiSi are formed.

3.3.2 Alloy Films

Three alloys of Ti_xV_{100-x} were investigated : $x = 20, 50$ and 80 . According to the Auger depth profiles the elements distribution in the as-deposited films is uniform. The X-Ray diffraction patterns of the alloys reveal BCC structures with lattice parameters that have intermediate values between those of β -Ti and V.

The reaction with Si is noted after 30min anneal at 600⁰C for the $Ti_{50}V_{50}$ alloy and at 550⁰C for the other two compositions. The alloys with $x = 80$ and 50 reveal non uniform redistribution following the interaction with Si; enrichment with titanium silicide at the substrate interface is observed, as shown in Fig.10 . The X-Ray analysis of the Ti- rich $Ti_{80}V_{20}$ sample following the 700 and 750⁰C annealings (see Fig. 11) shows three titanium silicides (Ti_5Si_3 , TiSi and $TiSi_2$) and the vanadium disilicide (VSi_2). Following the 850⁰C heat treatment, the metal rich silicide disappears. For the other two compositions ($Ti_{50}V_{50}$ and $Ti_{20}V_{80}$) only VSi_2 is revealed by the X-Ray analysis.

4. Discussion

The discussion of the experimental results will be focussed on four aspects : 1) The structure of the as-deposited films, 2) The reaction temperatures , 3) The reaction products , and 4) The components distribution as a result of the reaction.

4.1. Structure of the As-Deposited Films

The X-Ray diffractograms (both the patterns and the peak locations which vary with the amount of alloying) for all alloys in the as-deposited state clearly show mutual solubility of the components. And indeed this is expected for the Ta-W system since the equilibrium phase diagram is of complete solubility⁽²³⁾. From the phase diagram of Ta-V⁽²⁴⁾ at room temperature the Ta-rich composition of Ta₈₀V₂₀ is expected to be in a solid solution phase, while for the two other compositions studied (Ta₅₀V₅₀, Ta₂₀V₈₀) a mixture of this phase with a σ phase is expected. However, for high temperatures (>1322°C) complete solubility should be obtained for all compositions. For the Ti-V system the phase diagram⁽²³⁾ at room temperature predicts complete solubility for the Ti₅₀V₅₀ and Ti₂₀V₈₀ alloys and a mixture with an α - Ti phase for the Ti-rich composition. Here again at high temperatures (>600°C) complete solubility is expected also for the latter alloy. The experimental observations for all alloys in the as-deposited state are the detection of a single phase of a solid solution, namely, the high temperature rather than the room temperature structure is- obtained for Ta-V and Ti-V . A similar result is observed for the Ti film in the bilayer sample where the high temperature structure of BCC β -Ti is obtained rather than the hexagonal α -Ti . These results are not surprising

(we observed it also for the Ni-Cr system ⁽⁸⁾) since it is well established that the deposition process is not an equilibrium one and it can freeze higher temperature structures ⁽²⁵⁾.

4.2 Reaction Temperatures

The temperatures (for 30 min anneals) where interaction with Si is observed by AES for the various compositions studied are summarized in Table I . (The alloys are organized so that the parameter x denotes the atomic concentration of the metal with the higher formation temperature). The formation temperatures for the single metals, as derived from the data for the bilayer structures, confirm earlier reports ⁽¹²⁾. The more interesting case is that of the alloys, where we observe for some compositions a delay in the reaction temperature compared to the pure metal with $x = 0$. A delay (or reduction in reaction rate) can be attributed either to impurities or to effects of the alloying. The slowing down of silicide formation by impurities such as O is not new and has been reported ⁽²⁶⁾. And indeed in a few cases in our study we have observed that presence of C (probably from inefficient trapping of oil from the diffusion pump used in the early stages of the research), prevented silicide formation probably by arresting the metal atoms in the form of carbide. (Indications of presence of carbides were found in the line shape of the Auger transition of carbon for those samples). But for the samples summarized in Table I with the delay in reaction temperature, no impurities that could be blamed for this behavior were detected either in the film or at the substrate interface. We interpret the delay in silicide formation as resulting from the alloying recalling that for all alloys studied our X-Ray results prove that the as-deposited films are in the form of a solid solution.

The logical approach to analyze the alloying effects is first to see what is the expected behavior according to thermodynamics, namely to consider the driving force leading to the dissociation of the solid solution. The analysis presented in ref. 2, 4 can be implemented also in our case. In Fig.12 an idealized sketch of free energy vs. composition diagram of a binary system A-B is presented. Assuming that B is the metal with the lower silicide formation temperature (V in Ta-V, Ti in Ti-V, and Ta in Ta-W), then the depletion of B from the A-B solution in order to react with Si will increase or decrease the free energy of the alloy according to the alloy composition in the directions of the arrows in Fig.12. One can see that an increase in ΔG for A rich and a decrease for B-rich compositions is expected, thus the first case is less thermodynamically favored. Namely, we can explain on thermodynamical background the retardation of silicide formation of the metal with lower formation temperature in alloys where this element is the minority component. This may explain the increase in the formation temperature for $X \geq 50$ of the W_xTa_{100-x} and Ta_xV_{100-x} alloys (Table I) and possibly also the case of $Ti_{50}V_{50}$. Such an argumentation was used in earlier studies to explain the increase in silicide formation temperatures of near noble metals for near-noble refractory metals alloys (Pd-V⁽⁴⁾, Pd-W^(2,7), Ni-Cr⁽⁸⁾). In another case, Ir-V, silicide formation was slowed down by intermetallic components consisting of both metals^(27,28). However, the role of thermodynamics may not be so important in thin film interactions under conditions far from equilibrium, and changes in reaction rate may be related also to other effects such as mechanical stresses or changes in diffusion mechanism due to modifications in the composition and structure of the matrix.

4.3 Reaction Products

The reaction products for the bilayer structures are the expected silicides, confirming earlier reports for the separate interaction of each of the elements with Si⁽¹²⁾. However, for the alloys there are some deviations from the simple expectation to observe each of the elements to react separately with Si. Thus for example for reacted Ti₅₀V₅₀ we observe only VSi₂ reflections without those of titanium silicide. Such an observation should first be compared With the predictions of a ternary phase diagram of the Ti-V-Si system which is unavailable. However, Nowotny et al.,⁽²⁹⁾ studied the pseudo-binary compound (TiSi₂)_x-(VSi₂)_{100-x} for various x at high temperatures (>1350°C) and found that the hexagonal lattice of VSi₂ can dissolve up to 85 molar percents of TiSi₂. These high temperature bulk results may explain the missing reflections of Ti-silicides observed at 750-850°C. A similar result is obtained for Ta₅₀V₅₀ where following 850°C annealing no reflections of VSi₂ are found and those of TaSi₂ are shifted in their positions. Again it may be explained by dissolution of VSi₂ in the TaSi₂ lattice.

Another effect of the alloying on the reaction products is the appearance of metal rich silicides M₅Si₃ (Such as Ta₅Si₃ or Ti₅Si₃). Such compounds are usually not obtained for the reaction of thin films of a refractory metal with Si, but are stabilized by the presence of C⁽¹⁸⁾ (e.g. for the interaction of Ti_xC with Si⁽³⁰⁾) or when the Si supply is limited (e.g. cosputtered Ta or Ti with Si on SiO₂⁽¹⁾). The first case is also noted in this work where V₅Si₃ is found for the V/Ti bilayer in the outer region of the vanadium that is loaded with C (Fig. 9a) . But alloying a refractory metal with another refractory metal apparantly also stabilizes the M₅Si₃ phase; it is observed for all three alloy systems reacting with Si when no impurities were detected. Whether this is a kinetic effect or is expected by thermodynamics (we

recall again that ternary phase diagrams are not available) has not been determined within the frames of the present work and deserves further studies. Some support to the kinetic assumption is found by the fact that the metal rich phases are stable only in a small range of temperatures and disappear following higher temperature anneals.

Although we observe alloying to affect the reaction products by stabilizing M_5Si_3 phases and by dissolving some silicides in the lattice of others, no ternary compounds have been detected by us. The appearance of a ternary may be expected for Ta-W due to the close atomic sizes of Ta and W and their similar electronic configurations; however to the best of our knowledge such compounds were not detected even in the case of bulk samples. Again the lack of ternary phase diagram does not enable to comment whether they are expected at all. Usually the interaction of thin alloy films with Si does not lead to production of ternary compounds; they are found only in a few cases. For alloys consisting of two refractory metals, the interaction of Ti-W on Si is reported ⁽¹⁰⁾ to yield such a compound.

4.4 Components Distribution

For the Ta-V and Ta-W bilayer structures each of the layers reacts separately with Si without interdiffusion between the metals and thus structures of $TaSi_2/VSi_2/Si$, $VSi_2/TaSi_2/Si$, $TaSi_2/WSi_2/Si$ and $WSi_2/TaSi_2/S$ are finally obtained. Since for these metals silicide growth is dominated by Si outdiffusion ⁽¹²⁾ this result is not surprising. Therefore we are also not surprised to observe a uniform distribution of the components for the reacted Ta alloys, Ta_xV_{100-x} and Ta_xW_{100-x} .

The case of Ti-V differs from the other two systems. For the bilayer structures one observes Ti penetration through the V layer; for Ti/V/Si inwards diffusion to form Ti silicide adjacent to the substrate is observed, and for V/Ti/Si some outwards diffusion to form Ti oxide is noted. The driving force is of course the reduction in free energy by the formation of Ti silicide or oxide, and the mechanism is probably via grain boundary diffusion. We assume this mechanism since already for the as-deposited films we observe presence of some Ti in the V layer, and the occurrence of this phenomenon at such low temperatures (the substrate was not deliberately heated during deposition and its temperature rise is estimated to be $\sim 60^{\circ}\text{C}$) rules out any other transport mechanism. It is assumed that this mechanism is dominating also at the range of temperatures of $600\text{--}850^{\circ}\text{C}$ when the solid state reactions take place. It is interesting to note that for bulk diffusion at higher temperatures the diffusion of V in Ti is faster than that of Ti in V⁽³¹⁾.

The relatively fast permeation of Ti through the V layer can also explain the Ti accumulation near the substrate observed for the Ti-V alloys. Thus although both metals belong to the same group of refractory metals where silicide growth is dominated by Si outdiffusion, partial spacial phase separation is found, similarly to the case of the alloys consisting of a near noble and a refractory metal. In the latter case the phase separation was attributed to different diffusion mechanisms for silicide growth of both types of metals. Our results seem to indicate that some metal diffusion cannot be ruled out for Ti silicide growth, and in fact this can also explain its low formation temperature relative to other refractory metals. We recall that some

accumulation of CrSi_2 adjacent to the substrate for another refractory-refractory alloy (Ta-Cr) has also recently been reported⁽¹¹⁾ and again the formation temperature of CrSi_2 is relatively low.

4. Summary

The three studied systems of two refractory metals on Si share many properties. The as-deposited alloy films are in a single phase structure of a solid solution which delays in many cases the temperature of silicide formation. At the early stages of reaction metal rich compounds (M_5Si_3) appear, which later are replaced by the expected disilicides. However, for Ti_xV_{100-x} the titanium silicide is dissolved in the VSi_2 lattice, whereas for Ta_xV_{100-x} the VSi_2 is dissolved in the $TaSi_2$ lattice ; for the Ta_xW_{100-x} system there are conditions when both silicides are simultaneously detected. For all systems no ternary compounds are found. For the systems containing Ta the metals maintain their spacial distribution upon reaction with Si, whereas for Ti-V, both for the alloys and the bilayer structures, upon silicide formation Ti accumulation adjacent to the substrate is observed.

The results summarized so far were obtained during an intensive study which was unexpectedly limited by funding only to one year, and therefore could not encompass all aspects. Open interesting topics from the practical point of view for these alloys are the electrical properties of the alloy-Si interface, and their interaction with a top metallization of Al. And of course more metallurgical effort can yield results about reaction mechanisms and rates.

Acknowledgements

The authors are grateful to Dr.K.N.Tu (IBM-Yorktown Heights, NY) for enabling depositing the thin films in IBM's CSS deposition Laboratory (J.Cuomo and D.Yee are acknowledged) and to Dr.R.Brener (Technion - Usrael Institute of Technology), for carrying out the Auger measurements.

References

1. S.P. Murarka, J. Vac. Sci. Technol. 11, 775 (1980).
2. K.N. Tu, J. Vac. Sci. Technol. 19, 766 (1981).
3. J.O. Olowolafe, K.N. Tu and J. Angilello, J. Appl. Phys. 50, 6316 (1979).
4. J.W. Mayer, S.S. Lau and K.N. Tu, J. Appl. Phys. 50, 5855 (1979).
5. K.N. Tu, W.N. Hammer and J.O. Olowolafe, J. Appl. Phys. 51, 1663 (1980).
6. G. Ottaviani, K.N. Tu, J.W. Mayer and B.Y. Tsaur, Appl. Phys. Lett. 36, 331 (1980).
7. M. Eizenberg and K.N. Tu, J. Appl. Phys. 53, 1577 (1982).
8. A. Appelbaum, M. Eizenberg and R. Brener, J. Appl. Phys., to be published.
9. J.M. Harris, S.S. Lau, M.A. Nicolet, and R.S. Nowicki, J. Electrochem. Soc. 123, 120 (1976).
10. S.E. Babcock and K.N. Tu, J. Appl. Phys. 53, 6898 (1982).
11. C.J. Palmstrom, J. Gyulai and J.W. Mayer, J. Vac. Sci. Technol. A1, 452 (1983) - (was published during the period of current study).
12. K.N. Tu and J.W. Mayer, in: Thin Film Interdiffusion and Reactions (Edited by J.M. Poate, K.N. Tu, and J.W. Mayer) chap.10, Wiley, New York (1978).
13. JCPDS File card #8-53.
14. JCPDS File card # 11-195.
15. JCPDS File card # 6-0594.
16. JCPDS File card # 16-251.
17. JCPDS File card # 9-232.
18. W.B. Pearson, A Handbook of Lattice Spacings and Structures of Metals and Alloys, Pergamon Press, 1958.

19. JCPDS File card # 17-424.
20. JCPDS File card # 2-1120.
21. JCPDS File card # 8-379.
22. JCPDS File card # 29-1362.
23. C.J. Smithells, Metals Reference Book, Butterworths, London (1976).
24. R.P Elliott, Constitution of Binary Alloys, First Suppl. McGraw-Hill (1965).
25. K.L. Chopra, Thin Film Phenomena, McGraw-Hill (1969).
26. G. Ottaviani, J. Vac. Sci. Technol. 16, 1112 (1979).
27. M. Eizenberg and R. Brener, Thin Solid Films 89, 355 (1982).
28. M. Eizenberg, Phys. Stat. Sol. A.73, 483 (1982).
29. H. Nowotny, R. Machenschalk, R. Kiffer, and F. Benesorsky, Mh. Chem. 85, 241 (1954).
30. M. Eizenberg, S.P. Murarka and P.A. Heilmann, J. Appl. Phys. 54, 3195 (1983).
31. J.F. Murdock and C.J. McTargue , Acta Met. 16, 943 (1968).

III

Table I

x	$W_x Ta_{100-x}$	$Ta_x V_{100-x}$	$V_x Ti_{100-x}$
0	750°C	650°C	550°C
20	750°C	650°C	550°C
50	850°C	750°C	600°C
80	950°C	750°C	550°C
100	850°C	750°C	650°C

Formation temperatures (for 30 min anneals) of silicides for films studied.

x denotes atomic concentration of the metal with higher formation temperature.

Figures

- Fig. 1. AES depth profile of the bilayer structure Ta/W on Si in the as deposited state.
- Fig. 2. AES depth profile of Ta/W/Si following 30 min anneal at 850°C.
- Fig. 3. X-ray diffraction pattern of Ta/W/Si annealed at 850°C for 30 min.
- Fig. 4. Shift of (110) X-ray reflection due to alloying of $Ta_x W_{100-x}$ for $x = 0, 20, 50, 80$, and 100.
- Fig. 5. AES depth profile of $Ta_{80}W_{20}/Si$ sample after 30 min anneal at 850°C. Note the truncation of the Si signal at the substrate region.
- Fig. 6. X-ray diffraction pattern of $Ta_{80}W_{20}/Si$ sample annealed at 850°C for 30 min.
- Fig. 7. AES depth profile of $Ta_{80}V_{20}/Si$ following annealing at 750°C for 30 min.
- Fig. 8. AES depth profile of Ti/V/Si annealed at 750°C for 30 min. Ti penetration through the V layer is noted.
- Fig. 9. AES depth profile of V/Ti/Si annealed for 30 min. at a) 750°C, b) 850°C. The formation of a V rich silicide is noted in a.
- Fig. 10. AES depth profile of $Ti_{80}V_{20}/Si$ following anneal at 850°C for 30 min. Enrichment with Ti at the substrate interface is noted.
- Fig. 11. X-ray diffraction pattern of $Ti_{80}V_{20}/Si$ annealed at 750°C. The clear appearance of VSi_2 for the Ti-rich alloy is noted.
- Fig. 12. Schematic free energy curve of an A-B alloy. A is the element with a higher temperature of silicide formation. The arrows indicate the change in free energy due to depletion of B from an A-rich and a B-rich alloy.

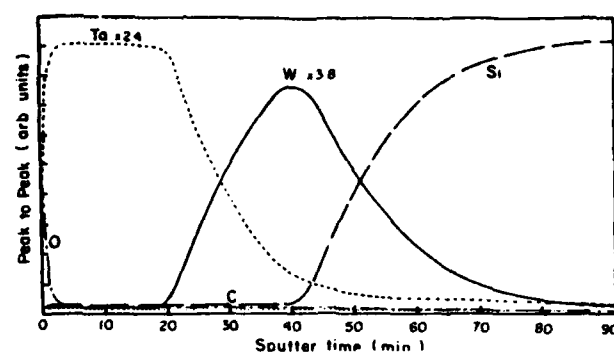


Figure 1

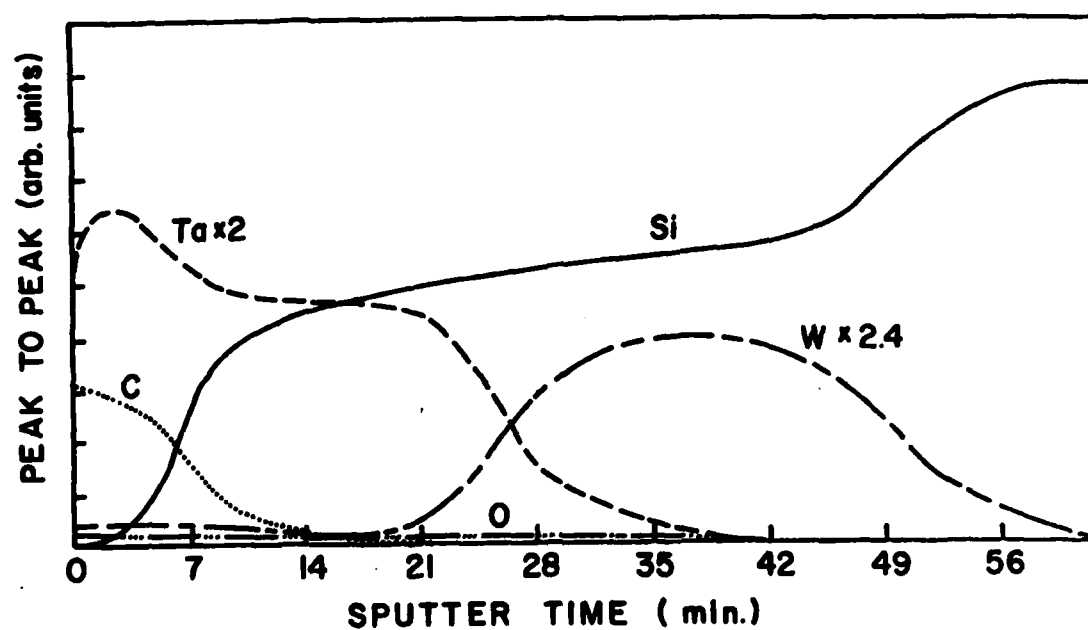


Figure 2

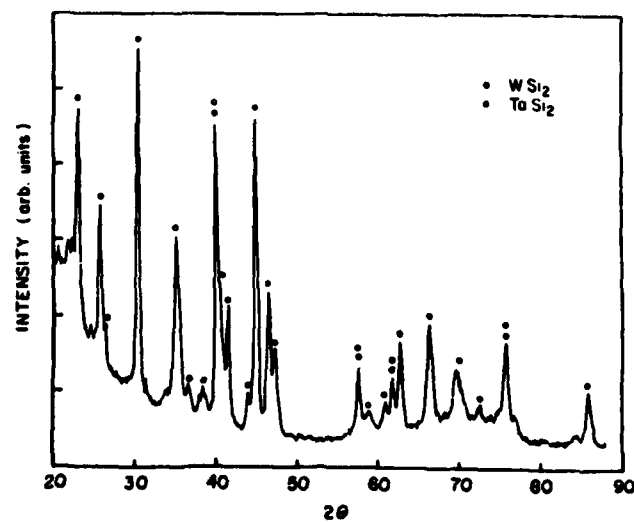


Figure 3

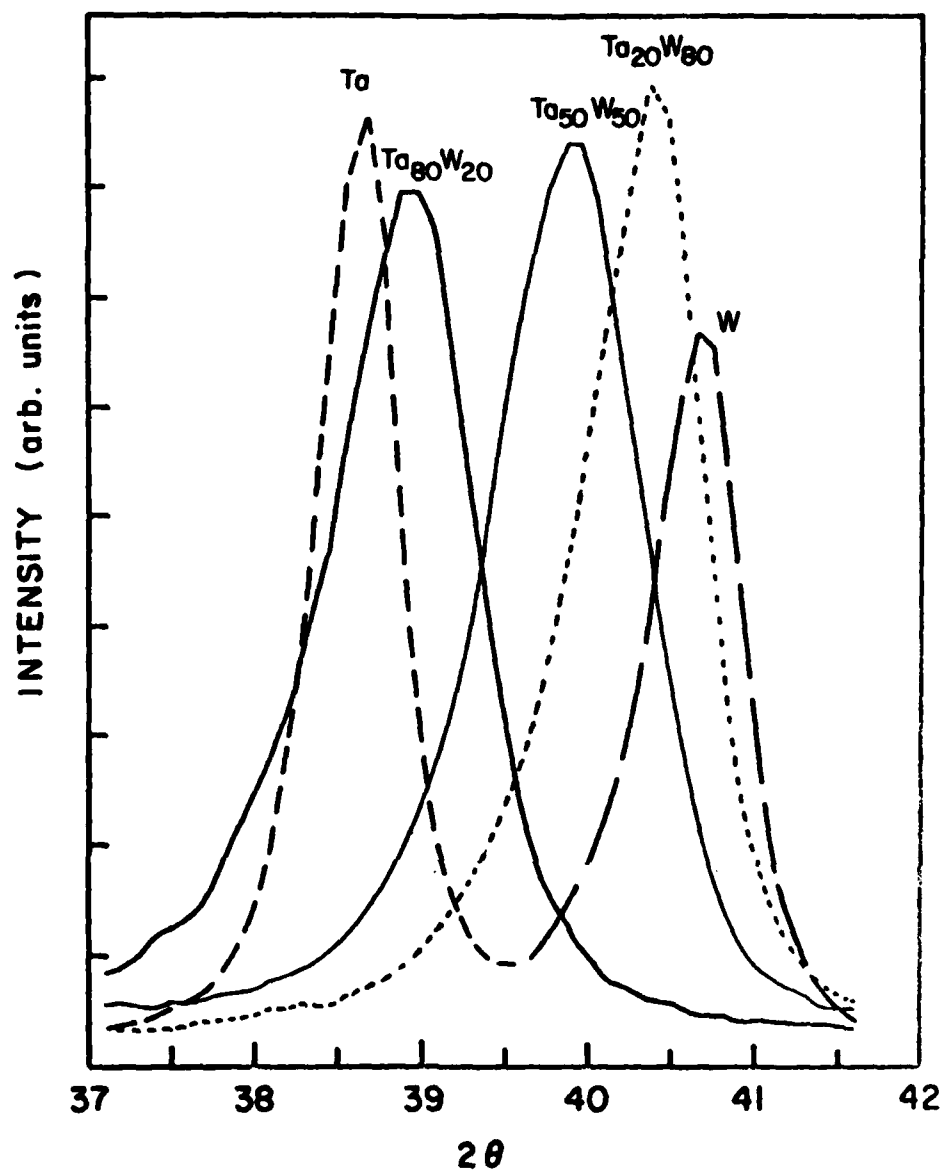


Figure 4

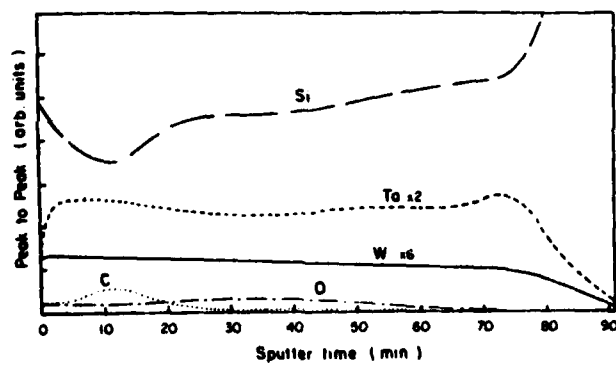


Figure 5

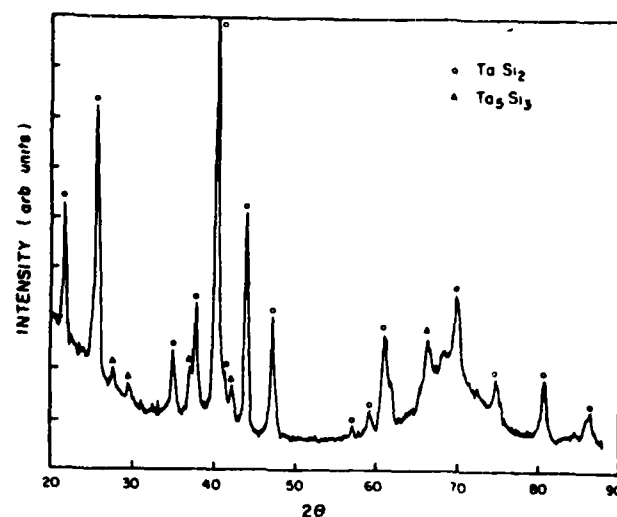


Figure 6

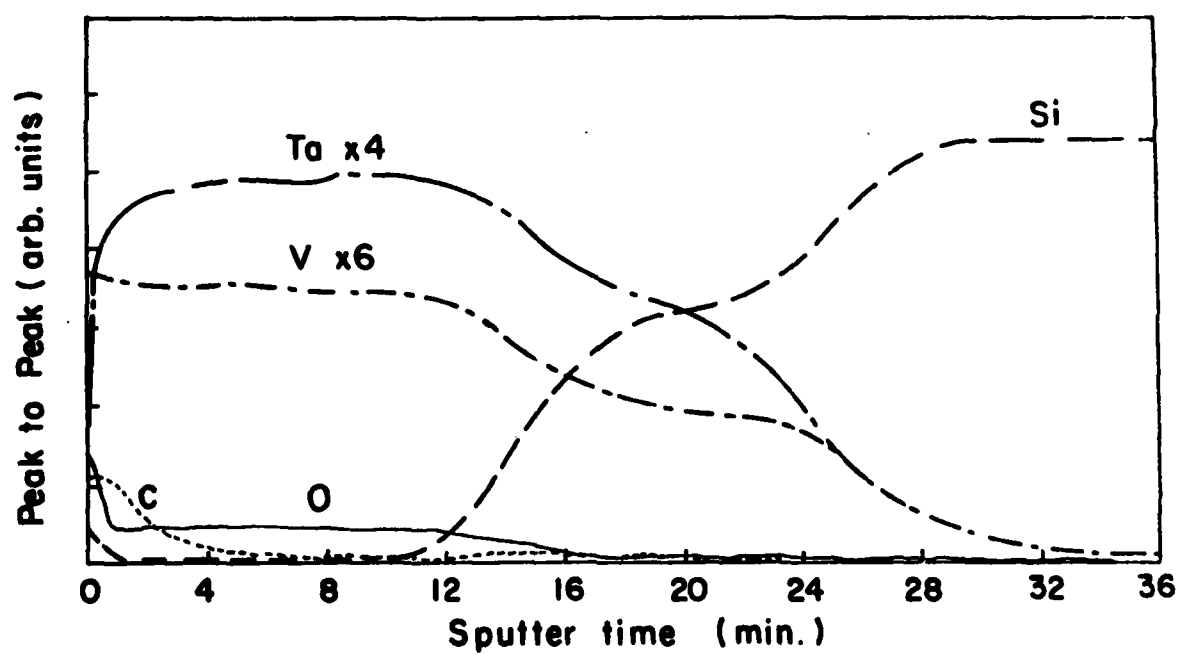


Figure 7

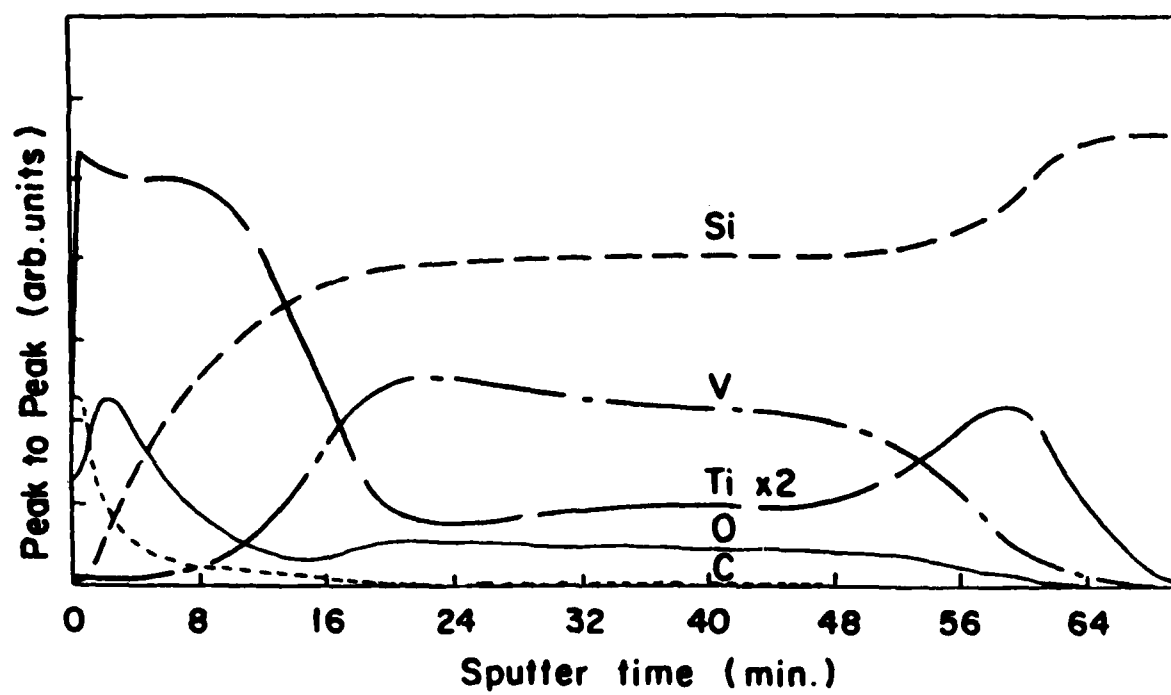


Figure 8

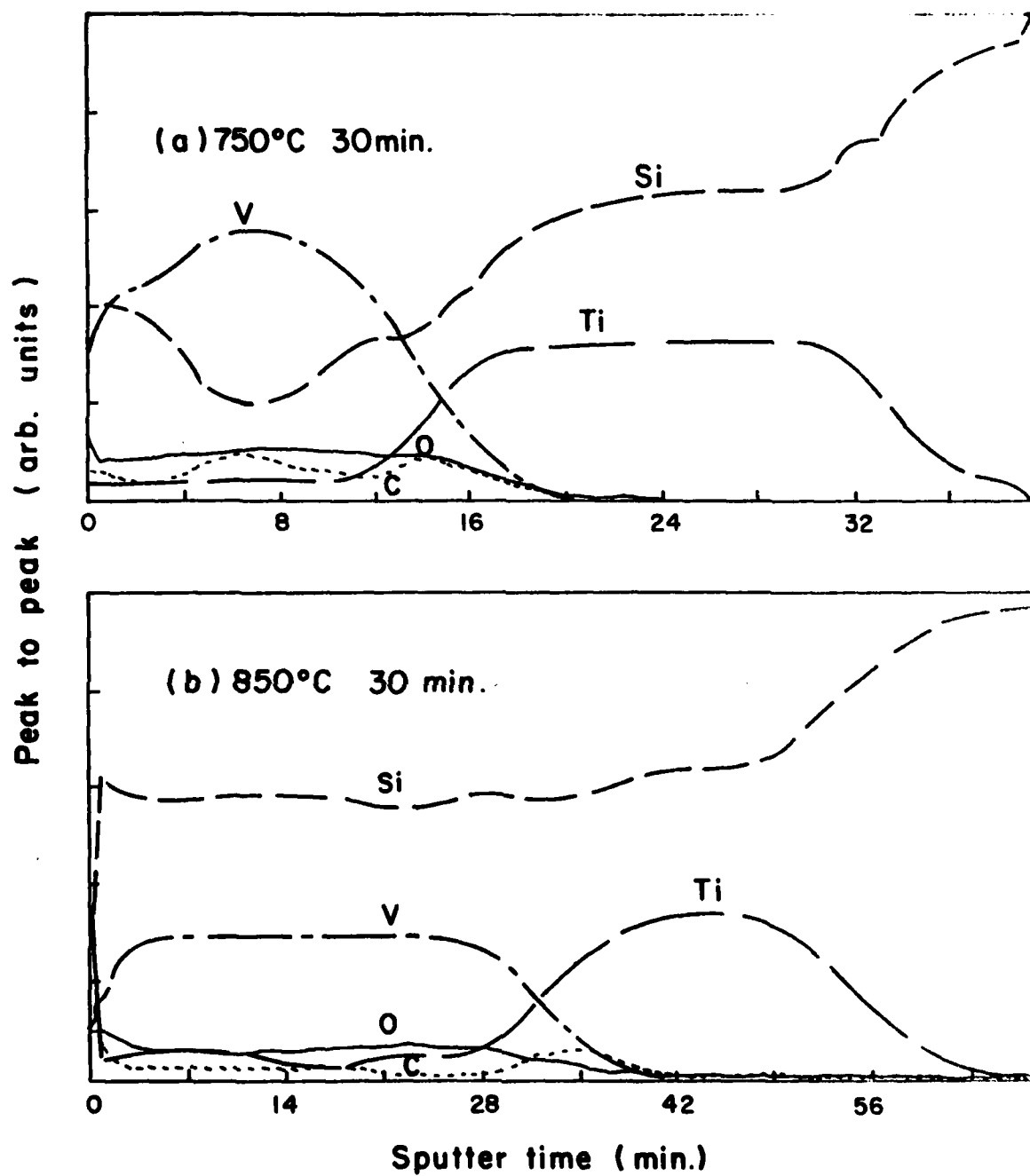


Figure 9

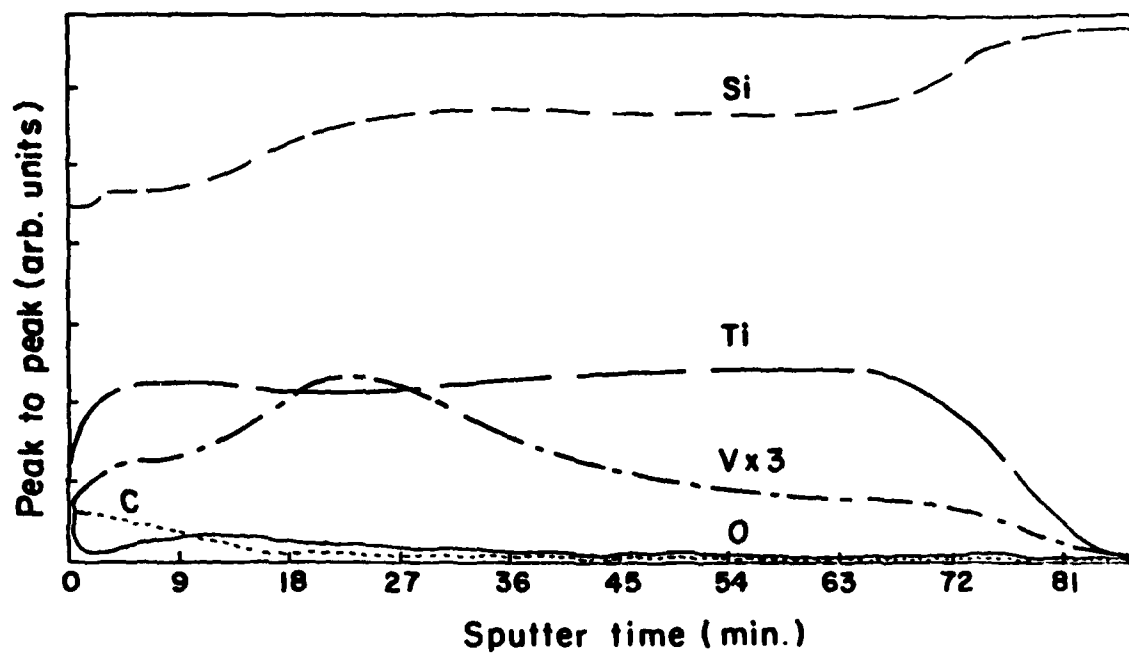


Figure 10

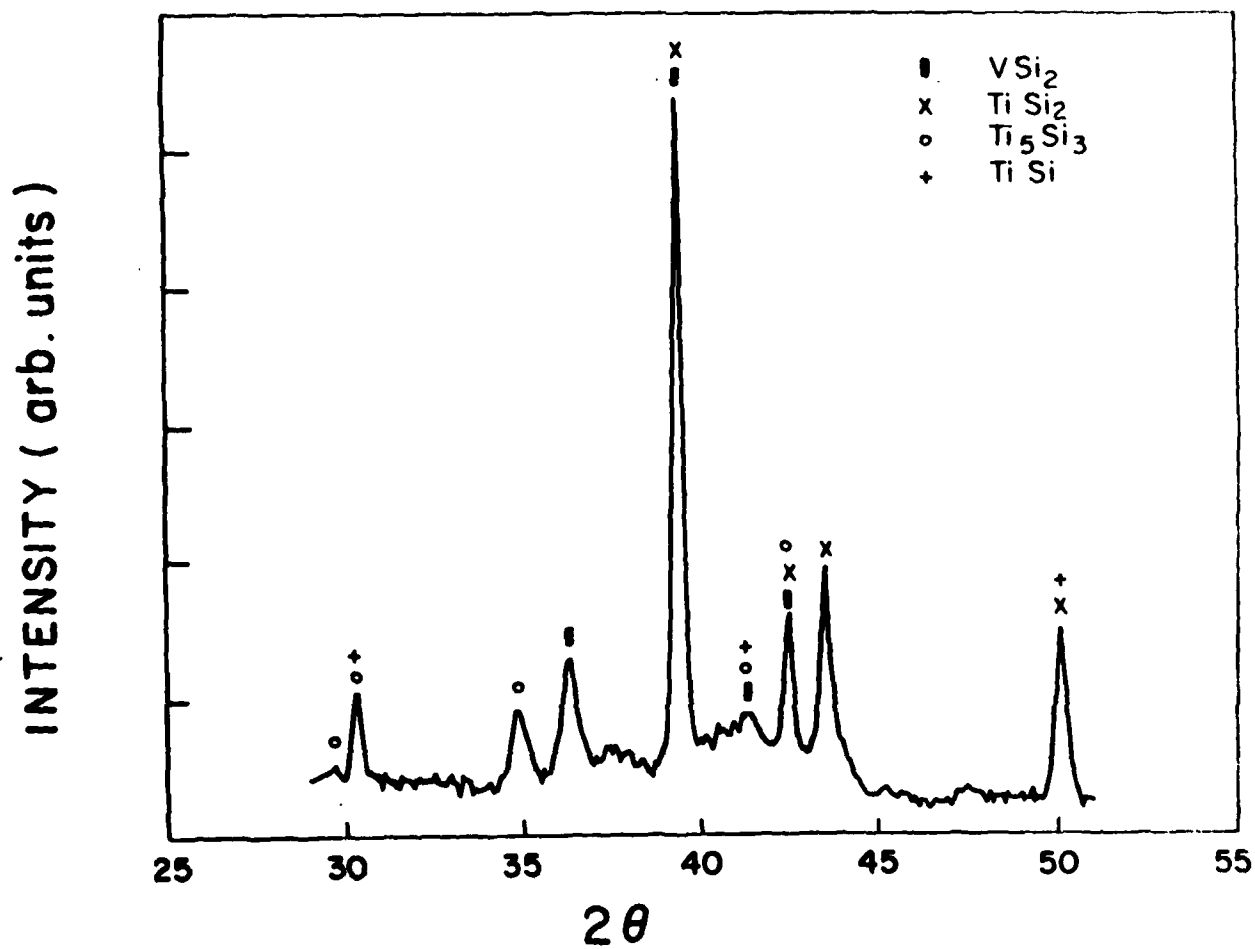


Figure 11

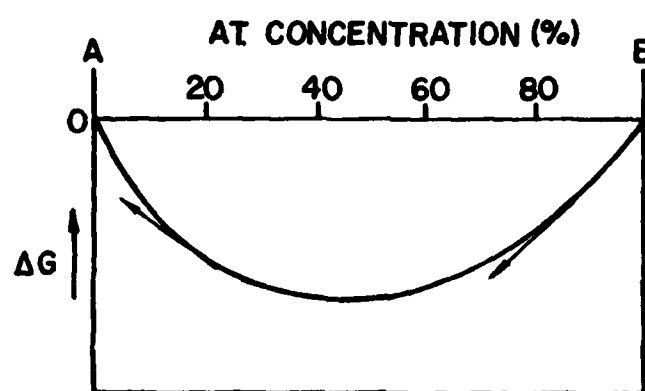


Figure 12

END